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Synthesis, X-ray molecular structure and electrochemical properties of a binuclear copper(I) complex with 2,7-diphenyl-azo-1,8-naphthyridine

Jean-Paul Collin*
Laboratoire de Chimie Organo-Minérale, UA au C.N.R.S. no. 422, Institut de Chimie, 1 rue Blaise Pascal, 67000 Strasbourg (France)

and Marie-Thérèse Youinou*
Laboratoire de Chimie des Métaux de Transition et de Catalyse, UA au C.N.R.S. no. 424, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg (France)

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Abstract

The synthesis of 2,7-diphenyl-azo-1,8-naphthyridine (dpan) and its reaction with copper(I) are described. The X-ray study of the new entity $[Cu_2(dpan)_3](BF_4)_2$ (**1**) reveals its molecular structure with two coppers separated by a distance of 3.526(1) Å. The distorted tetrahedral environment about each copper is provided by one bridging tetradentate dpan ligand and the two remaining bidentate dpan ligands. The stabilization of the molecule may, in part, be due to a stacking interaction between the two bidentate dpan ligands. The weak interaction between the copper(I) centers is confirmed by the electrochemical studies in CH_3CN. **1**$\cdot CH_2Cl_2,2C_6H_6,CH_3OH$ crystallizes in the triclinic space group $P\bar{1}$(No. 2), $a=15.443(7)$, $b=19.826(7)$, $c=13.763(6)$ Å, $\alpha=108.90(2)$, $\beta=113.21(2)$, $\gamma=73.12(2)°$, $Z=2$ and $V=3599$ Å^3 at -100 °C. The structure was refined to $R=6.6$ and $R_w=10.3\%$, respectively, using 5876 reflections with $I>3\sigma(I)$ and 973 variables.

Introduction

The coordination chemistry of 1,8-naphthyridine and its 2,7-disubstituted analogs displays a wide selection of coordination properties with various metal centers such as copper [1–5], nickel [6–10], rhenium [11], rhodium [12–17] or ruthenium [18–20]. The derivatives of 1,8-naphthyridine possessing functional groups at the 2 and 7 positions favor dinuclear complexes [12, 17], although other geometries have also been described [11, 16, 19]. The dinuclear structure of ruthenium complexes with the 1,8-naphthyridine-2,7-dicarboxylate ligand has recently been reported [20]. In particular, it was shown that the ancillary carboxylate groups play an important role in the stabilization of such mixed-valence species. Sacconi and co-workers have also demonstrated that mixed-valence $Cu^{II}Cu^{I}$ species are easily formed with the 4-methyl-1,8-naphthyridine bidentate ligand [2]. It was therefore of interest to investigate, in the presence of copper(I), the behavior of the related 2,7-diphenyl-azo-1,8-naphthyridine ligand (dpan, see Scheme 1), a potential bis-chelating compound. We describe herein a novel complex with dpan bound to two copper(I) centers and reveal its unexpected structure.

Experimental

Instrumentation and chemicals

^1H NMR spectra were acquired on a Bruker WP200SY instrument. Chemicals shifts are reported versus Me_4Si as internal standard. Cyclic voltammetry was carried out on a Bruker RI310 potentiostat connected to a XY Ifelec recorder. Potentials are reported relative to a saturated calomel electrode(SCE). FAB spectra were obtained by using a VG instrument ZAB-HF mass spectrometer. Elemental analyses of C, H and N were performed by the Service de l'Institut de Chimie de Strasbourg. All chemicals of reagent grade quality were used without purification. 1-Amino-7-hydroxo-1,8-naphthyridine, 2,7-dihydroxo-1,8-naphthyridine and 2,7-dichloro-1,8-naphthyridine were prepared by the procedure described by Newkome *et al.* [21]. $[Cu(CH_3CN)_4](BF_4)$ was obtained as previously reported [22].

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*Authors to whom correspondence should be addressed.

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2,7-Diamino-1,8-naphthyridine

The procedure used was a modification of that described by Brown and Dewar for the synthesis of 4,8-diamino-1,5-naphthyridine [23]. To a 500 ml three-necked flask fitted with a condenser, a thermometer and a glass inlet tube was added warm phenol (300 g). Ammonia gas was bubbled into the solution for 30 min after which 2,7-dichloro-1,8-naphthyridine (10 g, 0.005 mol) was added to the flask. The reaction mixture was heated to 170 °C for 20 h with a continuous flow of gas. After cooling, the phenol was distilled under reduced pressure. The resulting residue was dissolved in ethanol (200 ml), basified with 25% aqueous sodium hydroxide and filtered. The filtrate was concentrated and the residue purified by column chromatography (Al_2O_3, $MeOH/CH_2Cl_2$ 50:50) to give a pale green solid (7.5 g, 94%); m.p. 222–223 °C; ^1H NMR ($Me_2SO\text{-}d_6$): δ 7.56 (2H, d, $J = 8.4$ Hz), 6.36 (2H, d, $J = 8.4$ Hz), 6.22 (4H, s).

2,7-Diphenyl-azo-1,8-naphthyridine (dpan)

Nitrosobenzene (1.6 g, 15.6 mmol) was added as a solid to a suspension of 2,7-diamino-1,8-naphthyridine (0.4 g, 2.5 mmol) in an aqueous sodium hydroxide–benzene mixture (10 g of NaOH in 30 ml of water and 10 ml of benzene. Water (50 ml) was added to the cooled reaction mixture and the product was extracted into CH_2Cl_2(3×150 ml). Chromatography of the CH_2Cl_2 extract (Al_2O_3 and CH_2Cl_2 as solvent) yielded an orange powder upon concentration (0.42 g, 33%); m.p. 286–287 °C; ^1H NMR (CD_2Cl_2): δ 8.51 (2H, d, $J = 8.6$ Hz), 8.2 (4H, m), 8.11 (2H, d, $J = 8.6$ Hz), 7.68 (6H, m). ^{13}C NMR (CD_2Cl_2): δ 165.21, 152.82, 139.54, 133.10, 129.60, 124.82, 123.98, 113.75. FAB$^+$ (NBA): *m/z* 340 ($M+2$). *Anal.* Calc. for $C_{20}H_{14}N_6$: C, 70.99; H, 4.17; N, 24.83. Found: C, 70.78; H, 4.13; N, 24.66%. IR (KBr): 1597, 1550, 1481, 1465, 1187, 869, 813, 785, 690 cm^{-1}. UV λ_{max} (CH_2Cl_2): 244, 314, 365 nm.

$[Cu_2(dpan)_3](BF_4)_2$, ($\mathbf{1} \cdot CH_2Cl_2$)

$[Cu(CH_3CN)_4](BF_4)$ (0.28 g, 0.89 mmol) in 25 ml of degassed CH_3CN was added under argon to a dpan solution of CH_2Cl_2 (0.3 g, 0.89 mmol). The color of the solution turned immediately from orange to brown. The mixture was stirred for 1 h at room temperature and about 40 ml of CH_2Cl_2 were removed under vacuum. Degassed benzene (30 ml) was added and the solution was cooled overnight at 5 °C. The microcrystalline product obtained was collected by filtration and dried under vacuum (0.34 g, 54%). FAB$^+$ (NBA): *m/z* 1230.8 (calc. for $[Cu_2(dpan)_3](BF_4)^+$ 1230.8). *Anal.* Calc. for $[Cu_2(dpan)_3](BF_4)_2 \cdot CH_2Cl_2$: C, 52.28; H, 3.14; N, 18.0. Found: C, 52.18; H, 3.13; N, 18.5%. IR (KBr): 1584, 1482, 1371, 1311, 1194, 1156, 1125, 860, 772, 686 cm^{-1}. UV λ_{max} (CH_3CN): 311, 364, 420(sh) nm.

X-ray structure determination

Suitable black crystals of $\mathbf{1} \cdot CH_2Cl_2, 2C_6H_6, CH_3OH$ were obtained by diffusion of benzene into a CH_2Cl_2/CH_3OH solution of $\mathbf{1} \cdot CH_2Cl_2$ and were mounted at low temperature. Data were collected on a Philips PW1100/16 diffractometer equipped with a low temperature device using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal data and data collection parameters are summarized in Table 1. No significant changes were observed for three standard reflections monitored hourly during the data collection period. The Enraf-Nonius S.D.P. package [24] was used on a Microvax II computer for all calculations, except that a local program was employed for data reduction. The initial step-scan data was converted to intensities by the method of Lehmann–Larson [25] and then corrected

TABLE 1. X-ray experimental parameters for $\mathbf{1} \cdot CH_2Cl_2, 2C_6H_6, CH_3OH$

Chemical formula	$C_{74}H_{60}N_{18}OB_2F_8Cl_2Cu_2$
Formula weight	1589.0
Color	black
Crystal system	triclinic
a (Å)	15.443 (7)
b (Å)	19.826 (7)
c (Å)	13.763 (5)
α (°)	108.90 (2)
β (°)	113.21 (2)
γ (°)	73.12 (2)
V (Å^3)	3599
Z	2
D_{calc} (g cm^{-3})	1.466
Space group	$P\bar{1}$ (No. 2)
Radiation	Cu Kα (nickel filtered)
Wavelength (Å)	1.5418
μ (cm^{-1})	20.7
Crystal size (mm)	$0.18 \times 0.30 \times 0.40$
Temperature (°C)	-100
Diffractometer	Philips PW1100/16
Mode	$\theta/2\theta$ flying step-scan
Scan speed (°$^{-1}$)	0.024
Scan width (°)	$1.00 + 0.143\tan\theta$
Step width (°)	0.05
Theta limits (°)	3/50
Octants	$\pm h \pm k + l$
No. data collected	7407
No. data with $I > 3\sigma(I)$	5876
No. variables	973
Abs. min/max	0.81/1.18
$R(F)$	0.066
$R_w(F)$	0.103
ρ	0.08
GOF	2.23

for Lorentz, polarization and absorption factors with the latter being computed by the method of Walker and Stuart [26]. The structure was solved using the heavy atom method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were introduced at computed coordinates (C–H = 0.95 Å) with isotropic temperature factors $B(\mathrm{H}) = 1 + B_{\mathrm{eq}}(\mathrm{C})$ Å^2 but not refined. One of the BF_4^- anions showed signs of the usual rotational disorders and one of the fluorines was located over two positions for which half-occupancy was arbitrarily given. Four molecules of lattice solvents were identified as benzene (two molecules), dichloromethane and methanol. Final model involved anisotropic refinement of the non-hydrogen atoms. Full least-squares refinements converged to the R factors, shown in Table 1. Final difference maps revealed no significant maxima.

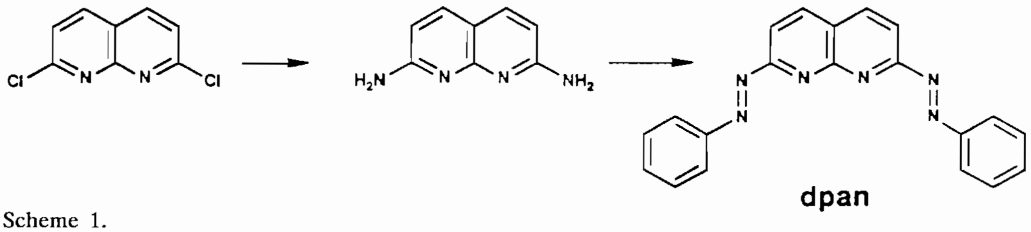
Results and discussion

To date, the use of 1,8-naphthyridine as a ligand has been greatly limited, certainly due to the very low yields generally obtained in the synthesis of such a ligand [27]. However, adequately chosen substituents on naphthyridine have proven to be a facile alternative and consequently the desired compounds could be obtained in a nearly quantitative yield. For this purpose, we used the strategy described by Newkome *et al.* for the synthesis of 2,7-dichloro-1,8-naphthyridine [21]. Functionalization of the 2 and 7 positions with two azo groups was then performed according to the following equation (Scheme 1).

Interestingly, the potentially tetradentate dpan ligand can be considered as a juxtaposition of two 2-phenyl-azo-pyridine groups. It is worth noting that for the typical *cis–trans* equilibrium of azo groups, the *trans* isomer is thermodynamically more stable and therefore we expect the same conformation in dpan. It was also of interest to compare the coordination properties of dpan with those of the 2-phenyl-azo-pyridine which is commonly recognized as a strong π-acceptor bidentate ligand, especially in the presence of copper and ruthenium [28–33]. Thus, the reactions of dpan and copper(I) were studied, varying the ligand to copper ratio. When the reaction mixture was carried out with a 1/1 ratio in a $CH_3CN/CH_2Cl_2/C_6H_6$ mixture, air-stable black crystals were obtained after a few days in a good yield. Unexpectedly, elemental analysis and FAB mass spectrum of the compound indicate the presence of three ligands per two copper ions corresponding to the formula $[Cu_2(dpan)_3](BF_4)_2$ (**1**). The proton NMR spectrum at room temperature showed only broad signals in the aromatic region, and no structural information could be thus obtained.

Crystals of **1** suitable for an X-ray structure determination were grown by diffusion of benzene into a CH_2Cl_2/CH_3OH solution of the complex. An ORTEP drawing is shown in Fig. 1 and selected bond distances and angles are given in Table 2. In the structure of **1**$\cdot CH_2Cl_2,2C_6H_6,CH_3OH$, the two copper centers, separated by a distance of 3.526(1) Å, are coordinated to three dpan ligands with azo groups in a *trans* position as expected; two of them act as bidentate whereas the third one is tetradentate and is involved in the coordination about both copper centers. The tetrahedral geometry about each copper is provided by four nitrogen atoms belonging to two distinct naphthyridine groups and to two azo groups, respectively. At each copper site, the Cu–N distances are only slightly different with an average value of 2.009(5) Å about Cul and 1.991(5) Å about Cu2. The six angles N–Cu–N within each distorted tetrahedral moiety range from 77.6(2) to 150.3(2)° for Cul and from 78.8(2) to 143.0(2)° for Cu2, the larger angles being obtained when either the two azo groups or the two naphthyridines belonging to distinct dpan are involved in the coordination.

Each pyridine group is planar with a maximum deviation of 0.042(6) Å. The three dpan ligands about the metal centers are arranged in such a way that the two bidentate dpan ligands are quasi-parallel with an angle of 5.4(9)° between the mean planes of the naphthyridines involving N10 and N15 and at a distance of about 3.33 Å allowing π-interaction. More interestingly, the dihedral angle of 50.9(1)° between the mean planes of the naphthyridines involving the tetradentate dpan (with N3 and N4) and one of the bidentate dpan (with N15) reflects the torsion of the complex in order to relieve ligand steric interactions. The result is a very distorted tetrahedral environment about both metal centers. Furthermore, such steric effects along with the stacking interaction provided by



Scheme 1.

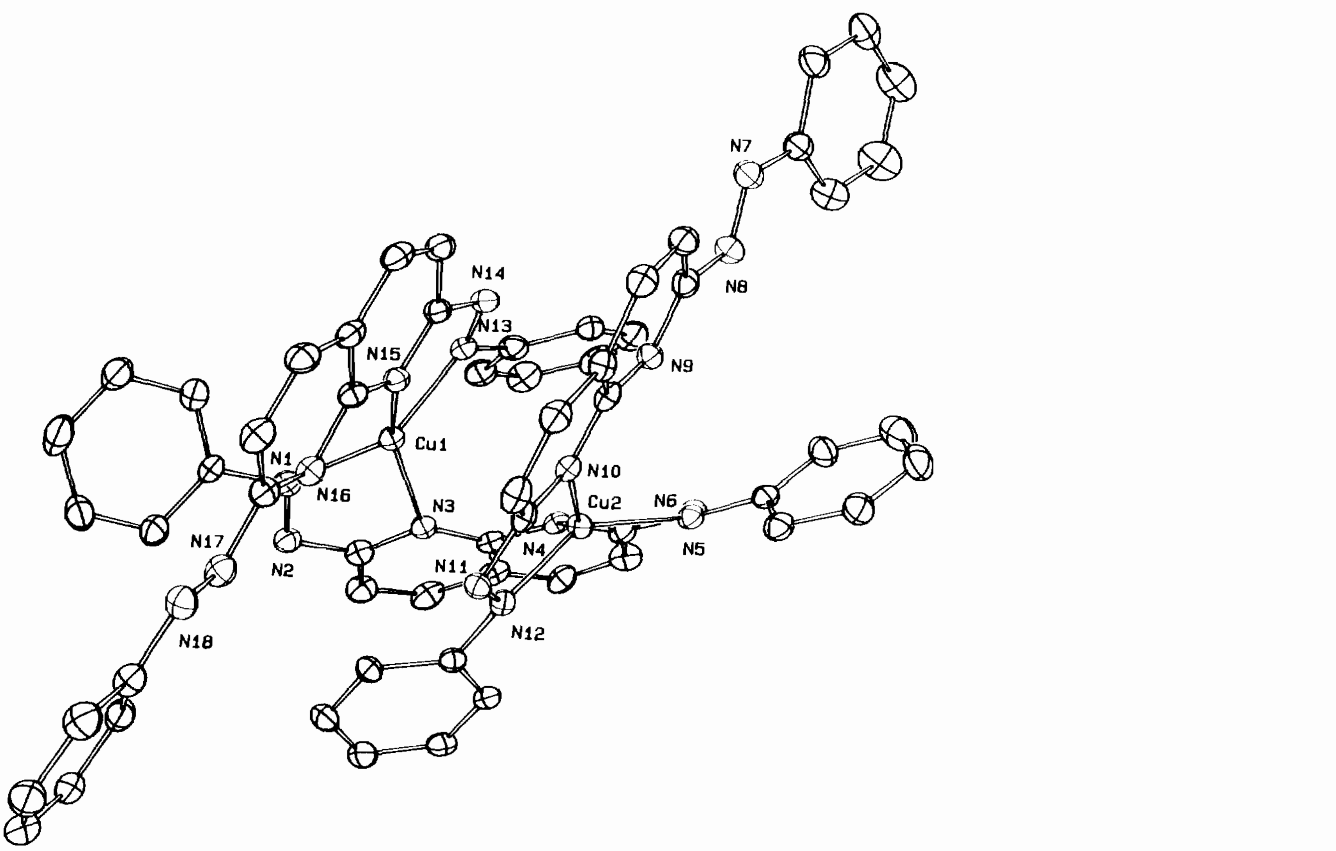


Fig. 1. ORTEP plot of one molecule of $1 \cdot CH_2Cl_2, 2C_6H_6, CH_3OH$ showing the numbering scheme used. Ellipsoïds are scaled to enclose 50% of the electronic density. Hydrogen atoms and solvents molecules are omitted.

TABLE 2. Selected distances (Å) and bond angles (°) for $1 \cdot CH_2Cl_2, 2C_6H_6, CH_3OH$

Distances (Å)		Bond angles (°)	
Cu1–N1	2.000 (6)	N1–Cu1–N3	79.4 (2)
Cu1–N3	2.015 (5)	N1–Cu1–N13	142.7 (2)
Cu1–N13	2.019 (6)	N1–Cu1–N15	114.2 (2)
Cu1–N15	2.002 (5)	N3–Cu1–N13	107.9 (2)
Cu2–N4	2.004 (5)	N3–Cu1–N15	150.3 (2)
Cu2–N6	1.982 (5)	N13–Cu1–N15	77.6 (2)
Cu2–N10	1.975 (5)	N4–Cu2–N6	79.5 (2)
Cu2–N12	2.002 (5)	N4–Cu2–N10	146.9 (2)
Cu1...Cu2	3.526 (1)	N4–Cu2–N12	110.9 (2)
		N6–Cu2–N10	112.4 (2)
		N6–Cu2–N12	143.0 (2)
		N10–Cu2–N12	78.8 (2)

e.s.d.s. are given in parentheses.

the bidentate dpan ligands may also be preventing the formation of the helicate structure.

In the tetradentate dpan ligand, another interesting feature is reflected by the similarity of the angles Cu1–N3--C9 and Cu2–N--C14, 152.7(3) and 153.5(3)°, respectively; this allows the two lone pairs of N3 and N4 to lie in a parallel fashion for coordination to the coppers.

The electrochemical redox behavior of free dpan and its copper(I) complex exhibit several interesting features. Figure 2 shows the cyclic voltammogram of dpan as well as **1** in CH_3CN with tetra-n-butylammonium perchlorate as supporting electrode. Dpan exhibits two quasi-reversible waves at -0.92 and -1.35 V which,

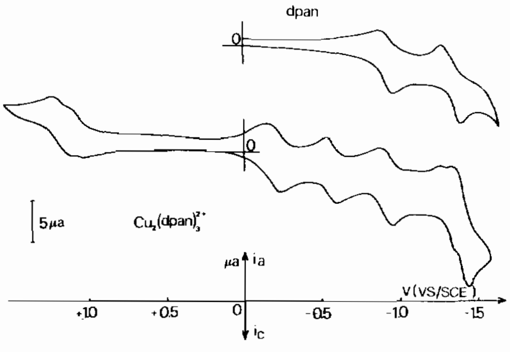


Fig. 2. Cyclic voltammograms of dpan and $1 \cdot CH_2Cl_2$ at the same concentration (5×10^{-4} M) in CH_3CN (0.1 M nBu_4ClO_4); glassy carbon electrode, sweep rate 100 mV s^{-1}.

Scheme 2.

by comparison with 2-phenyl-azo-pyridine [32] and analogous azo compounds [34], can be attributed to two two-electron transfers (Scheme 2). Such a scheme implies that there is no interaction between the two azo groups of dpan.

Interestingly, **1** undergoes five reversible redox couples between 1.0 and -1.5 V, with four of them in the negative potential range of -0.19, -0.55, -0.93 and -1.43 V. Cyclic voltammetry and linear-sweep voltammetry at a rotating disk electrode indicate that the first three processes each involve a two-electron transfer and the fourth one is a four-electron step. Similar to ruthenium complexes [29–32] with 2-phenyl-azo-pyridine, the azo groups are easier to reduce when coordinated. Thus, the two first waves at -0.19 and -0.55 V can be assigned to two two-electron reductions of the azo groups bound to the copper. The third wave at a potential of -0.93 V identical to that of the first reduction of the azo groups in the free ligand (-0.92 V) is due to the two unbound azo groups of **1**. The fourth four-electron process appears as an overlap of two two-electron waves; one is attributed to the second reduction of the non-coordinated azo groups (-1.32 V) whereas the other one represents the third electron transfer located on the coordinated azo groups. In the positive potential range, two overlapped one-electron waves are detected at about $+0.88$ and $+1.00$ V. Such high oxidation potentials demonstrate a strong stabilization of the copper(I) species, as seen with the copper(I) complex of 2-phenyl-azo-pyridine [28]. Furthermore, a separation of 120 mV between the redox couples shows that the $Cu^{II}Cu^{I}$ mixed-valence species may be considered as class II according to the classification of Robin and Day [35]. Although the two coppers are in close proximity ($d_{(Cu-Cu)} = 3.526(1)$ Å) and are coordinated to two nitrogen atoms of the same naphthyridine ligand, the resulting interaction between the metal centers is relatively weak. Such a phenomenon may be due to the steric interactions detected in the crystal structure.

Conclusions

We have synthesized and characterized a new dimeric copper(I) complex $[Cu_2(dpan)_3](BF_4)_2$ (**1**) in which one dpan acts as a bridging tetradentate ligand and the two remaining dpan as bidentate ligands, giving rise to an unexpected structure. Steric interactions between the three dpan ligands may be imposing strain in the molecule, preventing the formation of a helix. However, the existence of π-interaction between the bidentate dpan ligands seems to favor the present structure. Furthermore, **1** possesses a very interesting electrochemical behavior. In particular, the high oxidation potentials of **1** are indicative of highly stabilized copper(I) species. However, the small separation of the concerned potentials demonstrates only a relatively weak interaction between the two copper atoms through the bridging naphthyridine.

Supplementary material

Tables of complete bond lengths and angles, anisotropic thermal parameters, non-hydrogen and hydrogen atom coordinates, and tables of observed and calculated structure factors are available from the authors on request.

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